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Hydrogen bis[L-lysinium(2+)] dichloride perchlorate

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In the title compound, $2C_6H_{15}N_2O_2^+\cdot H^+\cdot ClO_4^-\cdot 2Cl^-$, the two mono- and dicationic lysinium molecules are held together by strong O—H···O hydrogen bonds. Both the perchlorate and chloride anions link molecules 1 and 2 through the α-amino and ε-amino groups into infinite chains along the a axis. The aggregation of the hydrophilic groups is along the $z = 0$ plane and that of hydrophobic is along the $z = \frac{1}{4}$ plane. Molecule 1 is engaged in a zigzag (Z1) head-to-tail sequence.

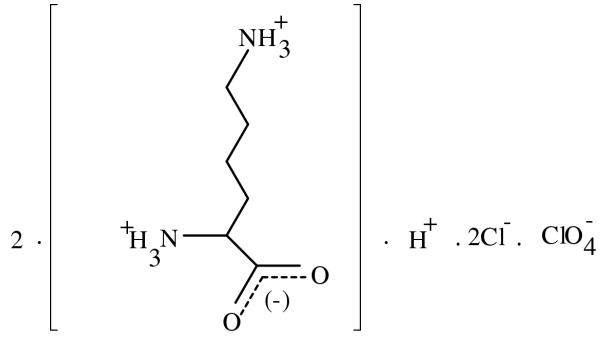
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.069
wR factor = 0.196
Data-to-parameter ratio = 11.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Lysine is one of the four amino acids having basic side chains. The crystal structure of L-lysine monohydrochloride dihydrate (Wright & Marsh, 1962; Koetzle *et al.*, 1972) and L-lysine semi maleate (Pratap *et al.*, 2000) have been reported. In the present study, the analysis of lysine hydrochloride reacted with perchloric acid, (I), was undertaken.



(I)

Both the lysinium molecules (1 and 2) in the asymmetric unit are cationic, with ε-amino groups accepting an H atom from hydrochloric acid. The H atom of the perchloric acid is liberated and bonded with molecule 2 and, as a result, the perchloric acid exists as perchlorate anion. The lysinium molecules have two planar configurations, the carboxyl group and aliphatic chain terminating at the ε-amino group. The amino N atom deviates from the carboxyl plane by 0.164 (4) and 0.126 (4) Å in lysinium molecules 1 and 2, which corresponds to the twisting of the C—N bond out of the carboxyl group by −6.0 (6) and 5.7 (7)°, respectively in molecule 1 and 2. This tendency of twisting of the C—N bond is found in various amino acids (Lakshminarayanan *et al.*, 1967). The average value of the four C—C—C angles is 112.6 and 117.1° in molecules 1 and 2, which is significantly greater than the

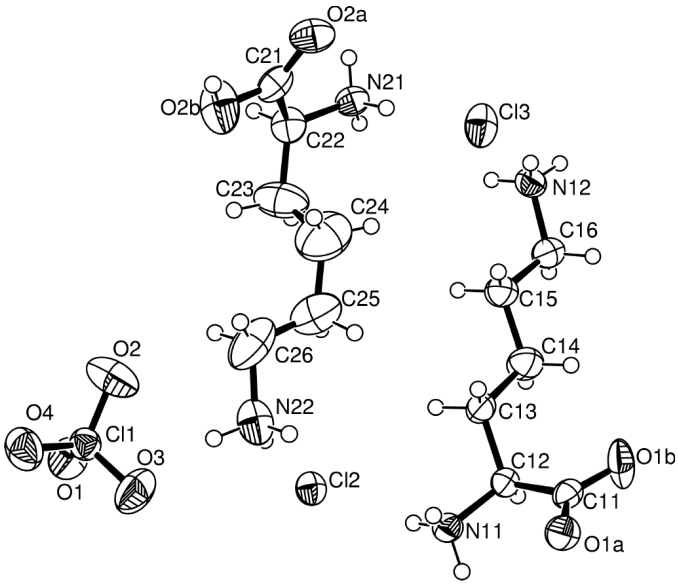


Figure 1
The structure of (I) showing the atomic numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

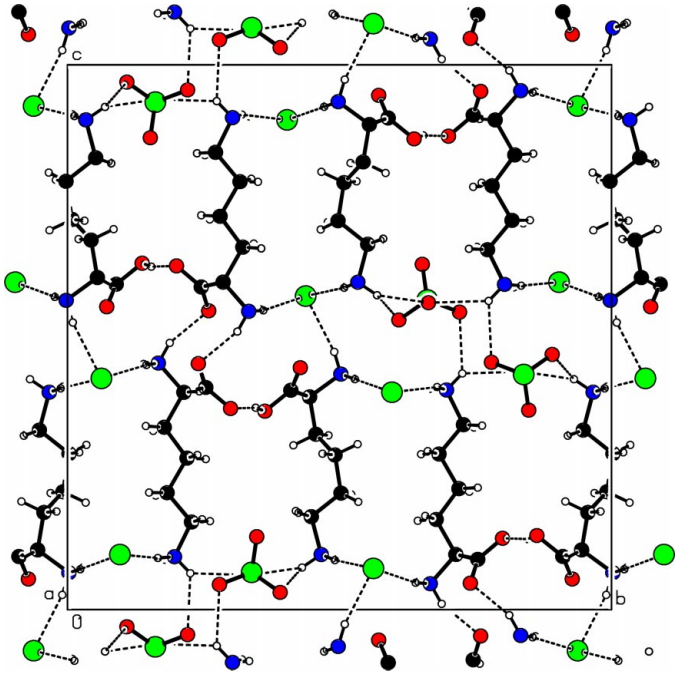


Figure 2
Packing of the molecules viewed down the *a* axis.

tetrahedral value. However, the angle $C^{\alpha}-C^{\beta}-C^{\gamma}$ of 114.0 (4) and 117.4 (8)° for both molecules 1 and 2 are appreciably large. Similar results are found in other amino acids and peptides, and this widening might be due to the steric effect of an atom hydrogen bonded to the NH_3^+ group (Leung & Marsh, 1958). While molecule 1, as expected, has a fully extended conformation for the side chain [χ^1 = −163.2 (6)°, χ^2 = -178.2 (6)°, χ^3 = 177.1 (7)° and χ^4 = −177.5 (6)°], molecule 2 does not have a fully extended conformation [χ^1 = 70.9 (10)°, χ^2 = 179.2 (8)°, χ^3 = −70.6 (14)° and χ^4 = −169.8 (9)°; Pratap *et al.*, 2000].

In the crystal, molecules 1 and 2 are bonded through a strong O—H···O hydrogen bond between the carboxyl O atoms. Lysinium molecule 1 is engaged in a zigzag (Z1) head-to-tail sequence since N11—H11*A*···O1*A*^{ii} [symmetry code: (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z$] connects two 2_1-related amino acids (Vijayan, 1988). The perchlorate anion links through the ε-amino group of four lysinium molecules extending in an infinite chain along the *a* axis. Both the chloride anions link lysinium molecules 1 and 2 through the α-amino and ε-amino groups into infinite chains along the *a* axis. The Cl2 atom, as acceptor, links (i) two lysinium molecules 1, through their α-amino groups and (ii) the two lysinium molecules 2, through the ε-amino groups. Similarly the Cl3 atom links (i) the two lysinium molecules 1 through the ε-amino groups and (ii) the two lysinium molecules 2 through the α-amino groups. The hydrophobic groups aggregate along the $z = \frac{1}{4}$ plane and the hydrophilic groups along the $z = 0$ plane.

Experimental

The title compound was crystallized in an aqueous solution from a 2:1 stoichiometric ratio of L-lysine hydrochloride and perchloric acid. Colorless transparent and plate-like crystals were grown.

Crystal data

$C_6H_{15}N_2O_2^+\cdot C_6H_{16}N_2O_2^{2+}\cdot ClO_4^-\cdot 2Cl^-$
M_r = 465.76
Orthorhombic, $P2_12_12_1$
a = 5.0264 (6) Å
b = 20.822 (2) Å
c = 20.897 (2) Å
V = 2187.1 (4) Å^3
Z = 4
D_x = 1.415 Mg m^{-3}
D_m = 1.413 Mg m^{-3}
D_m measured by flotation in a mixture of carbon tetrachloride and xylene
Mo *Kα* radiation
Cell parameters from 25 reflections
θ = 11.3–13.2°
μ = 0.46 mm^{-1}
T = 293 (2) K
Plate, colorless
0.50 × 0.40 × 0.25 mm

Data collection

Enraf–Nonius sealed-tube diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.859, T_{max} = 0.891
3207 measured reflections
2905 independent reflections
2427 reflections with $I > 2\sigma(I)$
R_{int} = 0.069
θ_{max} = 25.0°
h = −1 → 5
k = −1 → 24
l = −2 → 24
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.196
S = 1.06
2905 reflections
246 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1519P)^2 + 0.4185P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.007 (2)
Absolute structure: Flack (1983)
Flack parameter = 0.04 (15)

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.236 (7)	O2*A*—C21	1.203 (7)
O1*B*—C11	1.250 (7)	O2*B*—C21	1.284 (8)
O1*A*—C11—C12—N11	−6.0 (6)	O2*A*—C21—C22—N21	5.7 (7)
N11—C12—C13—C14	−163.2 (6)	N21—C22—C23—C24	70.9 (10)
C12—C13—C14—C15	−178.2 (6)	C22—C23—C24—C25	179.2 (8)
C13—C14—C15—C16	177.1 (7)	C23—C24—C25—C26	−70.6 (14)
C14—C15—C16—N12	−177.5 (6)	C24—C25—C26—N22	−169.8 (9)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*B*—H2*B*···O1*B*^{i}	0.82	1.65	2.453 (7)	166
N11—H11*A*···O1*A*^{ii}	0.89	1.98	2.810 (5)	156
N11—H11*B*···Cl2	0.89	2.48	3.343 (5)	164
N11—H11*C*···Cl2^{iii}	0.89	2.53	3.410 (5)	170
N12—H12*A*···O4^{iv}	0.89	2.36	3.041 (6)	134
N12—H12*A*···O1^{v}	0.89	2.41	3.109 (7)	136
N12—H12*B*···Cl3	0.89	2.48	3.314 (5)	156
N12—H12*C*···Cl3^{vi}	0.89	2.34	3.223 (5)	170
N21—H21*A*···Cl3^{vi}	0.89	2.39	3.261 (4)	168
N21—H21*B*···Cl3	0.89	2.37	3.258 (5)	179
N21—H21*C*···Cl2^{iv}	0.89	2.41	3.284 (4)	168
N22—H22*A*···O1^{iii}	0.89	2.18	2.960 (7)	146
N22—H22*A*···O3	0.89	2.58	3.088 (8)	117
N22—H22*B*···Cl2^{iii}	0.89	2.40	3.289 (6)	174
N22—H22*C*···Cl2	0.89	2.34	3.220 (5)	168

Symmetry codes: (i) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $x-\frac{1}{2}, \frac{3}{2}-y, -z$; (iii) $1+x, y, z$; (iv) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (v) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vi) $x-1, y, z$.

All H atoms were fixed by geometric constraints and were allowed to ride on the attached atom. Intensities for 225 Friedel pairs were measured, resulting in a Flack parameter of 0.04 (15). Atoms C23, C24, C25 and C26 showed large displacement amplitudes with unusual C—C distances, indicating disorder. Since a satisfactory disorder model was not found, these atoms were refined by constraining the bond distances involving them.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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